

TENT COOPERATION TRE. Y

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner
 US Department of Commerce
 United States Patent and Trademark
 Office, PCT
 2011 South Clark Place Room
 CP2/5C24
 Arlington, VA 22202
 ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 19 June 2001 (19.06.01)	
International application No. PCT/GB00/03347	Applicant's or agent's file reference DPW/AH/S654
International filing date (day/month/year) 01 September 2000 (01.09.00)	Priority date (day/month/year) 04 September 1999 (04.09.99)
Applicant RODDIS, James	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

03 April 2001 (03.04.01)

☐ in a notice effecting later election filed with the International Bureau on:2. The election ☒ was☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

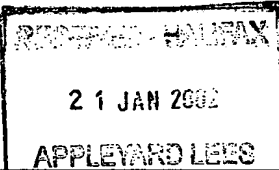
The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Zakaria EL KHODARY Telephone No.: (41-22) 338.83.38
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From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

WADDINGTON, Richard et al.
APPLEYARD LEES
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PTO/PCT Rec'd 25 FEB 2002



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NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT
(PCT Rule 71.1)

Date of mailing
(day/month/year) 18.01.2002

Applicant's or agent's file reference
RW/S654

IMPORTANT NOTIFICATION

International application No.
PCT/GB00/03347

International filing date (day/month/year)
01/09/2000

Priority date (day/month/year)
04/09/1999

Applicant
SHEFFIELD HALLAM UNIVERSITY et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

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PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference RW/S654		FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/GB00/03347	International filing date (day/month/year) 01/09/2000	Priority date (day/month/year) 04/09/1999	
International Patent Classification (IPC) or national classification and IPC C08K3/40			
Applicant SHEFFIELD HALLAM UNIVERSITY et al.			
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of sheets.</p>			
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input type="checkbox"/> Certain defects in the international application VIII <input checked="" type="checkbox"/> Certain observations on the international application 			
Date of submission of the demand 03/04/2001		Date of completion of this report 18.01.2002	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized officer Kaul-Buchberger, E Telephone No. +49 89 2399 8296	



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB00/03347

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-27 as originally filed

Claims, No.:

1-26 originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB00/03347

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	9-11,18-20,25,26
	No:	Claims	1-8,12-17,21-24
Inventive step (IS)	Yes:	Claims	
	No:	Claims	9-11,18-20,25,26
Industrial applicability (IA)	Yes:	Claims	1-26
	No:	Claims	

2. Citations and explanations see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB00/03347

Re It m V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability: citations and explanations supporting such statement

1. Reference is made to the following documents:
D1 = DATABASE WPI, Section Ch, Week 198229
Derwent Publications Ltd., London, GB;
Class A32, AN 1982-61619E
XP002152164 & ZA-A-8102389
D2 = DE-A-19845050
D3 = US-A-3808170
- 2.1. Document D1, which is considered to represent the most relevant state of the art, discloses a composition comprising a mixture of a non-matted particulate material (e.g. glass, preferably crushed or smashed glass, sand, crushed porcelain,...) and a thermosetting resin (esp. epoxy resin). For instance broken bottles can be used and the compositions can be used to form e.g. wall and ceiling panels.
- 2.2. Therefore, the subject-matter of claims 1, 5 and 17 lacks novelty in view of D1.
- 2.3. Document D2 discloses (table 1) an encapsulating material comprising an epoxy resin, a hardener, an accelerator and an anorganic filler (e.g. glass).
- 2.4. Therefore, the subject-matter of claims 1-8, 12-17, 22 and 23 lacks novelty in view of D2.
- 2.5. Document D3 discloses (example and claim 1) a prosthetic dental filling material comprising an epoxy resin, silane-treated glass granules, a catalyst and a catalyst accelerator. The silane-treated glass granules are mixed with the un-set resin and then the resin is allowed to set.

- 2.6. Therefore, the subject-matter of claims 1, 2, 4, 6-8, 12-17, 21-24 lacks novelty in view of D3.
- 2.7. The subject-matter of claim 9 differs from the disclosure of D1 in that at least 10 % w/w of the glass composite matrix comprises glass granules of a grain size of 4-6 mm.
- 3.1. There are no examples on file which show that the aforementioned distinguishing feature leads to an unexpected technical effect and, thus, the objective technical problem solved by said feature can only be regarded as to provide a further composition containing (waste) glass and a thermosetting resin.
- 3.2. If the person skilled in the art starting from D1 wanted to provide only an alternative, it would have been obvious to vary the amount and/or the size of the glass granules.
- 3.3. Therefore, the subject-matter of claim 9 does not meet the requirements of Article 33(3) PCT.
- 3.4. The additional features of claims 10, 11, 18-20, 25 and 26 are regarded as conventional and, thus, said claims do not meet the requirements of Article 33(3) PCT.
4. For all claims (1-26) industrial applicability is acknowledged.

Re Item VIII

Certain observations on the international application

1. The wording "waste glass" is unclear, since it seems not to be possible to decide in the product whether waste glass or other glass has been used. Therefore, claim 5 does not meet the requirements of Article 6 PCT.

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
15 March 2001 (15.03.2001)

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- (51) International Patent Classification⁷: C08K 3/40, 7/00 (74) Agents: WALSH, David, Patrick et al.; Appleyard Lees, 15 Clare Road, Halifax HX1 2HY (GB).
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9920843.1 4 September 1999 (04.09.1999) GB (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- (71) Applicant (*for all designated States except US*):
SHEFFIELD HALLAM UNIVERSITY [GB/GB];
City Campus, Howard Street, Sheffield S1 1WB (GB).
- (72) Inventor; and
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- Published:
— With international search report.
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: A GLASS COMPOSITE

(57) Abstract: The invention describes a solid glass composite comprising glass granules and a binder resin which may be used in a wide range of applications, for example, flooring, furniture, lighting, work surfaces and architectural features.

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A GLASS COMPOSITE

The present invention relates to a glass composite and, in particular, but not exclusively, a glass composite which
5 utilises waste glass from consumer, automotive and construction sources.

Research is increasingly being directed to the recycling
10 problems of waste glass from various industries and from domestic sources. Recycling of waste glass for many industries necessitates purification of the glass for its subsequent re-use. Nevertheless, due to the costs of purification, much of the waste glass is still committed
15 to undesirable landfill sites. New applications for the use of waste glass would alleviate much of the waste disposal problems associated with waste glass.

According to a first aspect of the present invention,
20 there is provided a solid glass composite matrix comprising glass granules and a binder resin which has set to bind the granules into a solid composite.

Preferably, the glass granules comprise between 40% and
25 90% w/w of the composite matrix, more preferably, between 65% and 85% w/w of the composite matrix, most preferably, between 75% and 85% w/w of the composite matrix.

When lower levels of glass granules are utilised other
30 bulking sources may be added to the resin to top up the glass level. For instance, sand may be added to the mix as a bulking agent and to increase silica levels. As much as 50% bulking agent may be used, more appropriately as

much as 30%, most appropriately, as much as 10%. Other potential bulking agents include mineral fillers such as bauxite and flint. However, the use of sand or other bulking agents is not preferred.

5 The percentage level of glass granules achievable in the composite is higher than is possible with non-resin binders. Typically, the level of glass granules is higher than 60% w/w of the composite matrix, more preferably,
10 higher than 70% w/w of the composite matrix, most preferably higher than 75% w/w of the composite matrix.

The glass granules may, preferably, comprise up to 75% w/w of the composite matrix, more preferably up to 80% w/w of the composite matrix, most preferably up to 85% w/w of the
15 composite matrix.

Preferably, the glass granules are derived from waste glass. Preferably, the waste glass has been crushed to
20 produce the granules. Typically, the crushed glass granules have been washed, dried and graded. Typically, the glass granules are obtained from crushed glass which may be derived from glass plate or ~~any other~~ convenient
~~source~~ ~~the~~ glass granules in the matrix have a grain
size substantially between 0.0mm and 20.0mm. Preferably,
at least 70% of the granules are between 0.0mm and 10.0mm,
more preferably at least 80%, most preferably, at least
30 90% of the granules are between 0.0mm and 10.0mm.

Preferably at least 50% w/w of the glass composite matrix comprises glass granules of grain size 0mm-6mm, more

preferably, at least 70% w/w of the glass composite matrix comprises glass granules of grain size 0mm-6mm, most preferably, at least 80% w/w of the glass composite matrix comprises glass granules of grain size between 0mm-6mm.

5

Preferably, at least 10% w/w of the glass composite matrix comprises glass granules of grain size 0mm-4mm, more preferably, at least 20% w/w of the glass composite matrix comprises granules of grain size 0mm-4mm, most preferably, at least 30% w/w of the glass composite matrix comprises granules of grain size 0-4mm.

10

Preferably, at least 10% w/w of the glass composite matrix comprises glass granules of grain size, 4mm-6mm, more preferably, at least 20% w/w of the glass composite matrix comprises glass granules of grain size 4mm-6mm, most preferably, at least 30% w/w of the glass composite matrix comprises glass granules of grain size 4-6mm.

15

Glass granules of between 6-10mm may also be present in the composite matrix. Granules between 6-10mm may be present at a level less than 50% w/w, more preferably, at a level less than 30% w/w, most preferably, at a level less than 25%.

25

Nevertheless, in some applications it is envisaged that 4-6mm granules or 6-10mm granules are present at up to 90% w/w, more preferably, up to 80% w/w, most preferably, up to 70% w/w of the composite matrix.

30

The waste glass may be derived from any suitable source including automotive, construction and consumer sources.

The glass may be clear or coloured or mixtures of colours and the colour of the glass grains may be utilised decoratively. In addition, larger decorative glass pieces greater than 10mm grain size may be added to the composite. In some cases, a decorative outer layer containing such pieces may be added to the base matrix. Such pieces larger than 10mm have not been taken into account herein in relation to the total weight of composite in stating the preferred % w/w of glass grains in the composite or the preferred % w/w of resin or other components in the composite.

Preferably, the matrix is ground after setting to provide a finish. Polishing may also be carried out. However, advantageously, with compositions of the invention, it is also envisaged that no grinding or secondary processes will be required. For instance, when producing tiles from moulds, it is possible to produce tiles from the moulds with high quality finish.

Preferably, the binder resin comprises between 5% w/w and 20% w/w of the composite matrix, more preferably between 7.5% and 17.5% of the composite matrix, most preferably, between 10% and 15% w/w of the composite matrix.

Preferably, the resin is polymeric and requires a curing agent or initiator to set.

Preferably, a coupling agent is present in the composite, to couple the glass and resin components together during setting of the composite, preferably, by chemical reaction with both components.

The coupling agent may be a silane coupling agent, preferably, an organo-functional silane coupling agent.

Preferably, the coupling agent is selected from a suitable
5 silane, titanate ester or zirco-aluminate.

The resin may be selected from any suitable binder resin including epoxy resins, polyurethane binders, unsaturated polyester binders and poly C₁-C₂ alkyl methacrylate
10 binders. Preferably, the polyalkyl methacrylate binder is polymethyl methacrylate.

A typical epoxy resin binder consists of the diglycidyl ether of bisphenol F or bisphenol A or mixtures thereof.
15 Typically, the average number molecular weight is less than or equal to 1000, more preferably 800, most preferably, 700. A reactive diluent may be added to suit viscosity requirements. Typically, the reactive diluents comprise mono-functional or di-functional aliphatic or
20 cycloaliphatic glycidyl ethers or esters. One or more of these may be mixed together in any proportions or used solely. A preferred diluent is a less viscous glycidyl ether such as C₁₂-C₁₄ alkyl glycidyl ether. The specific diluent may be varied to suit viscosity requirements.
25 Typically, the diluent is present at a level of 5-30% of the pre-cured resin, more preferably 10-25%.

The coupling agent may be present in the pre-cured resin at a level of 0.1-4.0% w/w, more preferably 0.5-3.0%, most
30 preferably 1.0-2.0% w/w.

The curing agent is preferably a UV stable moiety. A suitable UV stable curing agent for epoxy resin is octahydro-4,7-methano-1H-indendinethylamine.

5 Typical polyurethane binders comprise polyethers and/or polyester polyols together with aliphatic isocyanate curing agents.

10 Typical unsaturated polyester binders may comprise light stabilised orthophthalic or isophthalic resins together with a suitable initiator such as an organic peroxide. Typically, the alkyl methacrylate binders consist of aliphatic polyalkyl methacrylate copolymers or terpolymers together with a suitable initiator such as an organic
15 peroxide initiator.

Preferably, the binder resin is UV stable. Preferably the ratio of glass granules to binder resin and coupling agent is in the range of 6:1 to 3:1, more preferably 11:2 to
20 7:2, most preferably 5:1 to 4:1.

According to a second aspect of the present invention, there is provided a method of producing a glass composite comprising the steps of:-

25 contacting an aggregate of glass granules of average grain size less than 10mm with a binder resin,
mixing the granules into the un-set resin,
and allowing the resin to set so that the resin sets the granules into a solid composite matrix.

30

Preferably, the method of the second aspect may incorporate any one or more of the features of the first aspect of the invention.

Advantages of the use of resin together with waste glass granules include the low level of chemical reactivity between the resin and the silica in the glass so that the composite produced is highly stable. Furthermore, it has been found that it is possible to introduce higher levels of glass in a resin substrate than alternative substrates. Due to contamination risks, preferably, the resin is substantially solvent free.

The composite of the invention provides an impervious surface which may be UV stable and has excellent chemical resistance against typical materials such as:

oil, petrol, diesel, anti-freeze, salts, beverages, urine and dilute acids and alkalis.

Advantageously, prior to setting, the composite may be shaped in three dimensions and inconsistencies in the final set shape may be simply corrected by filling or polishing as is necessary. The casting techniques may be any of those known to those skilled in the art including vacuum-, pressure- and vibro-casting.

The composites of the invention may be utilised in many applications including:

internal and external flooring, furniture, lighting, work surfaces, architectural features such as skirting, architraves and sanitary work and the invention extends to methods of making such products using the method of the second aspect of the invention or the product of the first aspect. Furthermore, impervious examples of the product

may be utilised as material for commercial food preparation surfaces and chemical, including pharmaceutical, preparation surfaces. It is also envisaged that the invention may be used in applications which require high resistance to radiation such as natural, electro magnetic or nuclear radiation. Such applications include products and fittings in x-ray facilities in hospitals and sites within the nuclear industry. For such applications, it is preferred that the lead and/or barium level in the glass granules is sufficient to appreciably reduce the radiation transmission through the composite. A possible source of such glass granules with a high level of lead and/or barium is waste glass from VDU screens.

Preferably, the glass granules for screening applications has lead or barium or combined lead/barium levels at at least 3% by weight as a percentage of the raw constituent of the glass, more preferably at least 7% by weight, most preferably, at least 10% by weight. Preferably, the lead or barium levels or combined lead/barium levels for such applications are in the range 10-70% by weight in the glass granules, more preferably 20-70% by weight in the glass granules, most preferably, 40-70% by weight in the glass granules.

Further advantages of the composites of the invention are the high flexural strength and impact resistance. It is envisaged that these properties may be utilised in the production of body armour, including stab and ballistic body armour, either as part of a laminate with available materials or for total replacement of existing materials.

Tests have shown that materials according to the invention have excellent slip resistance, impact resistance, low thermal expansion, high compressive strength, high flexural strength, high tensile strength and high abrasion
5 resistance.

Internal and external flooring may be in the form of floor tiles. Preferably, the floor tiles are at least 3mm, more preferably at least 6mm. A preferred range is 4-35mm, a
10 more preferred range 6-25mm, a most preferred range is 8-20 mm. Such thickness ranges are considerably less than those employed for the equivalent concrete paving which they replace. Advantageously, the toughness and flexibility of the material allows much thinner floor
15 coverings to be used whereas concrete of equivalent thickness would crack due to its higher brittleness threshold.

Examples of the present invention will now be described.

20

Examples

The compositions of examples 1-10 are shown respectively in tables 1-5 and 16-20 which show the relative weight
25 percentages and absolute weights of the various constituents of the composites.

The epoxy resin in examples 1-10 comprises a blend of 80-84% bisphenol A & F, 15-19% C₁₂-C₁₄ alkyl glycidyl ether as
30 a diluent and 1% glycidoxy-functional silane coupling agent.

All these products produced high quality products after grinding and polishing.

The method of preparation of composite is as follows.

5

- i. The glass is weighed out in the correct percentages of each grain size and colour. (Usually 0-4mm, 4-6mm and 6-10mm, in colours green bottle, amber bottle, blue bottle and clear plate). See examples.
- 10 ii. The resin binder is mixed to the correct ratios (Base, catalyst and pigment), see examples, until an even dispersion is achieved.
- iii. The glass is then mixed thoroughly into the mixed resin binder.
- 15 iv. The "mix" is then either trowelled into moulds (for production of tiles or three dimensional items eg. furniture) or laid directly onto a preprepared floor surface as a screed.

Curing times @ 20°C

20

24 hours ... 70%

7 days ... 95%

28 days ... 100%

Although all curing times can be varied by using additives.

25

- v. Ideally, the mix should be "finished" in the period after 24h and before 48h, to the finish required (Currently, ground, polished or wire brushed).

30

Table 1 (Example 1)

Constituency	Percentage	Weight	Comments
Epoxy resin	12.61	378.34	Clear
Octahydro- 4,7-methano- 1H- indendimethyl amine.	6.42	192.60	Clear
Pigment RAL No. 4004 BS No.	0.03	0.94	
Aggregate mm 0.4	39.97	1200	Clear Plate
Aggregate mm 4-6	40.97	1230	Clear Plate
Aggregate mm 6-10	0	0	
Total	100	3001.88	

Table 2 (Example 2)

Constituency	Percentage	Weight	Comments
Epoxy resin	11.67	262.92	Clear
Octahydro- 4,7-methano- 1H- indendimethyl amine.	5.89	132.75	Clear
Pigment RAL No. 6019 Bs No.	0.12	2.60	
Aggregate mm 0.4	40.87	920.50	Clear Plate
Aggregate mm 4-6	41.45	933.75	Clear Plate
Aggregate mm 6-10	0	0	
Total	100	2252.52	

Table 3 (Example 3)

Constituency	Percentage	Weight	Comments
Epoxy resin	13.11	996.87	Clear
Octahydro- 4,7-methano- 1H- indendimethyl amine.	6.35	483	Clear
Pigment RAL No. 9003 BS No.	0.13	9.87	
Aggregate mm 0-4	35.31	2685.00	Clear Plate
Aggregate mm 4-6	45.10	3430.00	Clear Plate
Aggregate mm 6-10	0	0	
Total	100	7604.74	

Table 4 (a) (Example 4a)

Constituency	Percentage	Weight	Comments
Epoxy resin	10.95	93.68	Clear
Octahydro- 4,7-methano- 1H- indendimethyl amine.	5.27	45.05	Clear
Pigment RAL No. 9003	0.32	2.73	
Aggregates 0.4mm	58.13	497.25	Blue
4-6mm	25.34	216.75	Blue
6-10mm	0.00	0.00	
Total	100	855.46	

Table 4(b) (Example 4b)

Octahydro- 4,7-methano- 1H- indendimethyl amine.			
RAL No. 9003			
0.4mm			
4-6mm	1.98	30.00	Green
6-10mm			Blue
			Easy to trowel

Table 5

Constituency	Percentage	Weight	Comments
Epoxy resin	14.04	120.15	Clear
Octahydro- 4,7-methano- 1H- indendimethyl amine.	6.85	58.65	Clear
Pigment			
RAL No.9003	0.04	0.30	
5005	0.01	0.10	
BS No.			
Aggregates			
0-4mm	19.87	170.00	Clear Plate
4-6mm	38.74	331.50	Clear plate
	0.58	5.00	Green
6-10mm	19.87	170.00	
Total	100.00	855.70	

- 5 Tables 6-10 reveal grain size distribution for suitable glass granular samples which may be used with resins in accordance with the present invention.

Table 6Breakdown of Glass Samples

Grain Size (mm)	Mass (g)	Percentage
2-3.15	293.30	29.33
1-2	400.30	40.03
0.71-1	97.10	9.71
0.5-0.71	62.90	6.29
0.25-0.5	76.50	7.65
0-0.25	69.90	6.99

5

Table7

Grain Size (mm)	Mass (g)	Percentage
3.15-4	5.00	0.50
2-3.15	244.70	24.47
1-2	338.50	33.85
0.71-1	102.00	10.20
0.5-0.71	79.20	7.92
0.25-0.5	109.50	10.95
0-0.25	121.10	12.11

Table 8

Grain Size (mm)	Mass (g)	Percentage
> 4	78.60	7.86
3.15-4	127.00	12.70
2-3.15	239.00	23.90
1-2	244.00	24.40
0.71-1	114.50	11.45
0.5-0.71	75.10	7.51
0.25-0.5	91.30	9.13
0-0.25	30.50	3.05

5

Table 9

Grain size (mm)	Mass (g)	Percentage
> 4	134.03	13.40
3.15-4	192.06	19.21
2-3.15	339.50	33.95
1-2	174.20	17.42
0.71-1	52.58	5.26
0.5-0.71	31.28	3.13
0.25-0.5	44.60	4.46
0-0.25	31.75	3.17

Table 10

Grain Size (mm)	Mass (g)	Percentage
> 4	112.00	11.20
3.15-4	172.00	17.20
2-3.15	315.55	31.56
1-2	200.00	20.00
0.71-1	77.00	7.70
0.5-0.71	46.00	4.60
0.25-0.5	49.50	4.95
0-0.25	28.00	2.80

5 Test examples 6-10 have compositions as set out in tables 16-20.

The test results on example 6-10 are shown in tables 11-15 respectively.

10

Table 11 shows the impact resistance of example 6 which has been carried out in four separate tests. The recorded penetration is very low given that a maximum indentation depth of 3mm is all that is required for a high (category
15 A) soundness level. Table 12 shows that the coefficient of expansion of example 7 is similar to steel which makes the material highly suitable for applications in combination with steel to minimise differential rates of expansion and contraction in variable temperature
20 environments.

Table 11

	Recorded Penetration
Test No 1	0.5mm
Test No 2	0.4mm
Test No 3	0.2mm
Test No 4	0.0mm

5 Table 12

	Mean Coefficient of
Test age 7 days	3.0×10^{-5}
Test age 28 days	4.2×10^{-5}

10 Table 13 shows that the flexural strength of example 8 is very high and this may give opportunities in combination with flexible backing surfaces or substrates such as soil or earth.

Table 13

15

	Flexural Strength (N/mm ²)
Test age 7 days	(See Note 1)
Test age 28 days	41.9 (see Note 2)

Note 1 - Test pieces flexed without failure, flexural strength can not be recorded.

20 Note 2 - Test pieces 1 and 3 had air bubbles on the fracture surface, test 2 flexed a long way before failure.

Table 14 shows a comparison of abrasion resistance with a concrete floor slab for example 9. The sample performs at a much higher level and shows improved abrasion resistance compared with concrete.

5

Table 14

	Mean Wear Depth	Results from an
Test Duration 2 hours	0.038mm	external concrete
Test Duration 1 hour	0.025mm	floor slab (For
		comparison)
Test Duration 15 minutes	0.00mm	1.21mm

10 Advanced humidity and resistance to liquids tests for example 1 were carried out. The resistance to humidity test comprised cyclic condensation between - 10°C and 40°C following BS 3900 Part F2: 1989. The resistance to liquids test was carried out using the water immersion
 15 method of BS 3900: Part G8: 1993. The example was found to have satisfactory resistance to water immersion and cyclic condensation at temperatures between -10°C and 40°C at 100% humidity.

Table 15 (Example 6)Impact Testing (Sample)

Constituency	Percentage	Weight	Comments
Epoxy resin	11.17	251.67	Clear
Octahydro- 4,7-methano- 1H- indendimethyl amine.	5.65	127.35	Clear
Pigment RAL No. 2010 BS No.	0.06	1.25	
Aggregates 0-4mm	42.66	960.97	Clear Plate
4-6mm	40.46	911.25	Clear Plate
6-10mm	0.00	0.00	
TOTAL	100.00	2252.49	

5

Table 16 (Example 7)

Coefficient of Thermal Expansion Sample

Constituency	Percentage	Weight	Comments
Epoxy resin	13.22	396.99	Clear
Octahydro- 4,7-methano- 1H- indendimethyl amine.	5.80	174.00	Clear
Pigment RAL No. 1014	0.03	0.99	
Aggregates	20.49	615.00	Green
0-4mm		615.00	Amber
4-6mm	19.99	600.00	Amber
	19.99	600.00	Green
Aggregate mm 6-10	0	0	
TOTAL	79.51	3001.98	

Table 17 (Example 8)
Flexural Strength Sample

Constituency	Percentage	Weight	Comments
Epoxy resin	11.17	251.67	Clear
Octahydro- 4,7-methano- 1H- indendimethyl amine.	5.65	127.35	Clear
Pigment RAL No. 2010	0.06	1.25	
Aggregates 0-4mm	42.66	960.97	Clear Plate
4-6mm	40.46	911.25	Clear Plate
6-10mm	0.00	0.00	
TOTAL	100.00	2252.49	

Table 18 (Example 9)Abrasion Testing Sample

Constituency	Percentage	Weight	Comments
Epoxy resin n	13.25	397.98	Clear
Octahydro- 4,7-methano- 1H- indendimethyl amine.	5.79	174.00	Clear
Pigment RAL No. 9003	0.07	1.98	
Aggregates 0-4mm	47.94	1440.00	Green
4-6mm	32.95	990.00	Green
6-10mm	0.00	0.00	
TOTAL	100.00	3003.96	

5

Table 19 (Example 10)

Coefficient of Friction Sample

Constituency	Percentage	Weight	Comments
Epoxy resin	11.17	251.67	Clear
Octahydro- 4,7-methano- 1H- indendimethyl amine.	5.65	127.35	Clear
Pigment RAL 2010	0.06	1.25	
Aggregates 0-4mm	42.66	960.97	Clear Plate
4-6mm	40.46	911.25	Clear Plate
6-10mm	0	0	
TOTAL	100.00	2252.49	

5

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated
5 otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the
10 foregoing embodiment(s). The invention extend to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so
15 disclosed.

CLAIMS

- 5 1. A solid glass composite matrix comprising glass granules and a binder resin which has set to bind the granules into a solid composite.
2. A solid glass composite matrix according to claim 1,
10 wherein the glass granules comprise between 40% and 90% w/w of the composite matrix.
3. A solid glass composite matrix according to either of claims 1 or 2, wherein other bulking sources are added
15 to the resin to top up the glass level.
4. A solid glass composite matrix according to any preceding claim, wherein the level of glass granules is higher than 60% w/w of the composite matrix.
20
5. A solid glass composite matrix according to any preceding claim, wherein the glass granules are derived from waste glass.
- 25 6. A solid glass composite matrix according to any preceding claim, wherein the glass granules in the matrix have a grain size substantially between 0.0mm and 20.0mm.
- 30 7. A solid glass composite matrix according to any preceding claim, wherein at least 50% w/w of the glass composite matrix comprises glass granules of grain size 0mm-6mm.

8. A solid glass composite matrix according to any preceding claim, wherein, at least 10% w/w of the glass composite matrix comprises glass granules of grain size 0mm-4mm.
9. A solid glass composite matrix according to any preceding claim, wherein at least 10% w/w of the glass composite matrix comprises glass granules of grain size, 4mm-6mm.
10. A solid glass composite matrix according to any preceding claim, wherein granules between 6-10mm are present at a level less than 50% w/w.
11. A solid glass composite matrix according to any preceding claim, wherein the matrix is ground after setting to provide a finish.
12. A solid glass composite matrix according to any preceding claim, wherein the binder resin comprises between 5% w/w and 20% w/w of the composite matrix.
13. A solid glass composite matrix according to any preceding claim, wherein the resin is polymeric and requires a curing agent or initiator to set.
14. A solid glass composite matrix according to any preceding claim, wherein a coupling agent is present in the composite, to couple the glass and resin components together during setting of the composite.

15. A solid glass composite matrix according to claim 14, wherein the coupling agent is a silane coupling agent.
- 5 16. A solid glass composite matrix according to either of claims 14 or 15, wherein the coupling agent is selected from a suitable silane, titanate ester or zirco-aluminate.
- 10 17. A solid glass composite matrix according to any preceding claim, wherein the resin is selected from any suitable binder resin including epoxy resins, polyurethane binders, unsaturated polyester binders and poly C₁-C₂ alkyl methacrylate binders.
- 15 18. A solid glass composite matrix according to any preceding claim, wherein a reactive diluent is added to suit viscosity requirements.
- 20 19. A solid glass composite matrix according to claim 18, wherein the reactive diluents comprise mono-functional or di-functional aliphatic or cycloaliphatic glycidyl ethers or esters.
- 25 20. A solid glass composite matrix according to either of claims 18 or 19, wherein the diluent is present at a level of 5-30% of the pre-cured resin.
- 30 21. A solid glass composite matrix according to any of claims 14 to 20, wherein the coupling agent is present in the pre-cured resin at a level of 0.1-4.0% w/w.

22. A solid glass composite matrix according to any of claims 13 to 21, wherein the curing agent is a UV stable moiety.
- 5 23. A solid glass composite matrix according to any of claims 14 to 22, wherein the ratio of glass granules to binder resin and coupling agent is in the range of 6:1 to 3:1.
- 10 24. A method of producing a glass composite comprising the steps of:-
contacting an aggregate of glass granules of average grain size less than 10mm with a binder resin,
mixing the granules into the un-set resin,
15 and allowing the resin to set so that the resin sets the granules into a solid composite matrix.
25. A solid glass composite matrix according to any preceding claim, wherein the glass granules for screening applications has lead or barium or combined
20 lead/barium levels at at least 3% by weight.
26. A solid glass composite matrix according to claim 25, wherein, the lead or barium levels or combined lead/barium levels for such applications are in the
25 range 10-70% by weight in the glass granules.

INTERNATIONAL SEARCH REPORT

Inte Application No
PCT/EP 00/03347

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08K3/40 C08K7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 198229 Derwent Publications Ltd., London, GB; Class A32, AN 1982-61619E XP002152164 & ZA 8 102 389 A (VAN TONDER C A J), 12 March 1982 (1982-03-12) abstract	1-26
X	DE 198 45 050 A (HITACHI CHEMICAL CO LTD) 8 April 1999 (1999-04-08) table 1 claims 1-4	1-26
X	US 3 808 170 A (ROGERS S) 30 April 1974 (1974-04-30) claims 1-15	1-26

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

7 November 2000

Date of mailing of the international search report

16/11/2000

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INTERNATIONAL SEARCH REPORT

Information on patent family members


Info: Application No

PCT/GB 00/03347

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
ZA 8102389	A	28-04-1982	NONE	
DE 19845050	A	08-04-1999	JP 11166106 A	22-06-1999
US 3808170	A	30-04-1974	NONE	

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference RW/S654		FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB00/03347	International filing date (day/month/year) 01/09/2000	Priority date (day/month/year) 04/09/1999	
International Patent Classification (IPC) or national classification and IPC C08K3/40			
Applicant SHEFFIELD HALLAM UNIVERSITY et al.			
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of sheets.</p>			
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none">I <input checked="" type="checkbox"/> Basis of the reportII <input type="checkbox"/> PriorityIII <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicabilityIV <input type="checkbox"/> Lack of unity of inventionV <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statementVI <input type="checkbox"/> Certain documents citedVII <input type="checkbox"/> Certain defects in the international applicationVIII <input checked="" type="checkbox"/> Certain observations on the international application			
Date of submission of the demand 03/04/2001		Date of completion of this report 18.01.2002	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized officer Kaul-Buchberger, E Telephone No. +49 89 2399 8296	



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB00/03347

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-27 as originally filed

Claims, No.:

1-26 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB00/03347

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	9-11,18-20,25,26
	No:	Claims	1-8,12-17,21-24
Inventive step (IS)	Yes:	Claims	
	No:	Claims	9-11,18-20,25,26
Industrial applicability (IA)	Yes:	Claims	1-26
	No:	Claims	

2. Citations and explanations see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

R It m V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Reference is made to the following documents:

D1 = DATABASE WPI, Section Ch, Week 198229

Derwent Publications Ltd., London, GB;

Class A32, AN 1982-61619E

XP002152164 & ZA-A-8102389

D2 = DE-A-19845050

D3 = US-A-3808170

- 2.1. Document D1, which is considered to represent the most relevant state of the art, discloses a composition comprising a mixture of a non-matted particulate material (e.g. glass, preferably crushed or smashed glass, sand, crushed porcelain,...) and a thermosetting resin (esp. epoxy resin). For instance broken bottles can be used and the compositions can be used to form e.g. wall and ceiling panels.
- 2.2. Therefore, the subject-matter of claims 1, 5 and 17 lacks novelty in view of D1.
- 2.3. Document D2 discloses (table 1) an encapsulating material comprising an epoxy resin, a hardener, an accelerator and an anorganic filler (e.g. glass).
- 2.4. Therefore, the subject-matter of claims 1-8, 12-17, 22 and 23 lacks novelty in view of D2.
- 2.5. Document D3 discloses (example and claim 1) a prosthetic dental filling material comprising an epoxy resin, silane-treated glass granules, a catalyst and a catalyst accelerator. The silane-treated glass granules are mixed with the un-set resin and then the resin is allowed to set.

- 2.6. Therefore, the subject-matter of claims 1, 2, 4, 6-8, 12-17, 21-24 lacks novelty in view of D3.
- 2.7. The subject-matter of claim 9 differs from the disclosure of D1 in that at least 10 % w/w of the glass composite matrix comprises glass granules of a grain size of 4-6 mm.
- 3.1. There are no examples on file which show that the aforementioned distinguishing feature leads to an unexpected technical effect and, thus, the objective technical problem solved by said feature can only be regarded as to provide a further composition containing (waste) glass and a thermosetting resin.
- 3.2. If the person skilled in the art starting from D1 wanted to provide only an alternative, it would have been obvious to vary the amount and/or the size of the glass granules.
- 3.3. Therefore, the subject-matter of claim 9 does not meet the requirements of Article 33(3) PCT.
- 3.4. The additional features of claims 10, 11, 18-20, 25 and 26 are regarded as conventional and, thus, said claims do not meet the requirements of Article 33(3) PCT.
4. For all claims (1-26) industrial applicability is acknowledged.

Re Item VIII

Certain observations on the international application

1. The wording "waste glass" is unclear, since it seems not to be possible to decide in the product whether waste glass or other glass has been used. Therefore, claim 5 does not meet the requirements of Article 6 PCT.